ASTIA DOCUMENT NO: AD 408 257
CONTRACT AF 61(052)-351

ARL 63-129
TN No. 90

TECHNICAL NOTE

SPIN COMPONENT ANALYSIS OF SINGLE DETERMINANT WAVE FUNCTIONS

by

Fukashi Sasaki and Kimio Ohno

Quantum Chemistry Group
For Research in Atomic, Molecular and Solid-State Theory
Uppsala University, Uppsala, Sweden

November 30, 1962

The research reported in this document
has been sponsored in part by the
AERONAUTICAL RESEARCH LABORATORY, OAR,
THROUGH THE EUROPEAN OFFICE, AEROSPACE RESEARCH,
UNITED STATES AIR FORCE.

ASTIA DOCUMENT NO: AD
CONTRACT AF 61(052)-351 TN No. 90

TECHNICAL NOTE

SPIN COMPONENT ANALYSIS OF SINGLE DETERMINANT WAVE FUNCTIONS

by

Fukashi Sasaki * and Kimio Ohno *

Quantum Chemistry Group
For Research in Atomic, Molecular and Solid-State Theory
Uppsala University, Uppsala, Sweden

* On leave from: Department of Physics, Faculty of Science, University of Tokyo, Tokyo, Japan.

November 30, 1962

The research reported in this document
has been sponsored in part by the
AERONAUTICAL RESEARCH LABORATORY, OAR,
THROUGH THE EUROPEAN OFFICE, AEROSPACE RESEARCH,
UNITED STATES AIR FORCE.

1. INTRODUCTION

A single-determinant form for wave functions has been used extensively in the quantum mechanics of many-electron systems.

In the usual Hartree-Fock method, single-determinant wave functions are used with a restriction that two electrons with spins α and β are put into the same space orbital. A single-determinant wave function with this restriction is an eigenfunction of the total spin operator S^2 . The Hartree--Fock method has proved to be very useful in the theory of atoms, molecules and solids.

In the unrestricted Hartree-Fock method, single-determinant wave functions without the above mentioned restriction are used. This allows us to treat, in a compact form, the exchange polarization and the correlation of electrons with antiparallel spins. However, the unrestricted Hartree-Fock method has a disadvantage. Wave functions used in the method are in general not eigenfunctions of the total spin but are linear combinations of eigenfunctions which have different eigenvalues.

It is of some interest to see how much of each spin eigenfunction is contained in the single-determinant wave function.

2. FORMULATION OF THE PROBLEM

Any antisymmetric wave function of an N-electron system can be written in the following form,

$$\Phi(\xi_1,\xi_2,\cdots,\xi_N) = \mathcal{A}\left(\Psi(\mathbb{r}_1,\mathbb{r}_2,\cdots,\mathbb{r}_N)\Theta(\sigma_1,\sigma_2,\cdots,\sigma_N)\right) , \qquad (2.1)$$

where ξ_i stands for the space and spin coordinates $\mathbb{r}_i$ and σ_i respectively of the i-th electron. $\mathcal{A}$ is the idempotent antisymmetrizing operator. By using permutation operators P and their parities ε_P , the antisymmetrizing operator $\mathcal{A}$ is expressed as

$$\mathcal{A} = \frac{1}{N!}\sum_P \varepsilon_P P . \qquad (2.2)$$

The wave function Φ is in general a linear combination of pure spin states:

$$\Phi = \sum \Phi_{S,M} , \qquad (2.3)$$

where $\Phi_{S,M}$ is an eigenfunction of S^2 and S_z with the eigenvalues $S(S+1)$ and M respectively ($\hbar = 1$).

This decomposition is of physical importance if the Hamiltonian does not involve spin operators. An expectation value of a spin-free operator f can be expressed as

$$\begin{aligned} \langle f \rangle &= \frac{\langle \Phi, f \Phi \rangle}{\langle \Phi, \Phi \rangle} \\ &= \sum_{S,M} \omega_{S,M} \langle f \rangle_{S,M} , \end{aligned} \tag{2.4}$$

where

$$\omega_{S,M} = \frac{\langle \Phi_{S,M}, \Phi_{S,M} \rangle}{\langle \Phi, \Phi \rangle} \geqq 0 , \quad \left(\sum_{S,M} \omega_{S,M} = 1 \right) \tag{2.5}$$

and

$$\langle f \rangle_{S,M} = \frac{\langle \Phi_{S,M}, f \Phi_{S,M} \rangle}{\langle \Phi_{S,M}, \Phi_{S,M} \rangle} , \tag{2.6}$$

when $\langle \Phi_{S,M} , \Phi_{S,M} \rangle$ is not zero. When the Hamiltonian of the system is spin-free, we have

$$E = \sum_{S,M} \omega_{S,M} E_{S,M} . \tag{2.7}$$

This equation shows that at least one of the energy expectation values $E_{S,M}$ is lower than E unless all $E_{S,M}$ are equal to E. By selecting from Φ a suitable spin component $\Phi_{S,M}$, we have a wave function which is not only a spin eigenfunction but which has a lower energy expectation value.

The analysis is also useful in interpreting the function Φ, (2.1). This is in some cases (e.g. a single Slater determinant) much easier to handle than its components $\Phi_{S,M}$. If we know the values of $\omega_{S,M}$ and $\langle f \rangle_{S,M}$, we can better interpret the nature of the simple form (2.1). One of the basic problems here is to determine the weight $\omega_{S,M}$.

In the following we shall investigate a special case in which the spin part Θ of the wave function (2.1) is a simple product of spin functions $\gamma_i(\sigma_i)$ which are either $\alpha(\sigma_i)$ or $\beta(\sigma_i)$:

$$\Theta(\sigma_1, \sigma_2, \cdots, \sigma_N) = \gamma_1(\sigma_1)\gamma_2(\sigma_2) \cdots \gamma_N(\sigma_N) . \tag{2.8}$$

The spin function Θ is an eigenfunction of S_z . If we denote the number of α and β functions in (2.8) by N_α and N_β respectively, the eigenvalue of S_z (M) is expressed as

$$M = \frac{1}{2}(N_\alpha - N_\beta) \ . \tag{2.9}$$

In order to evaluate $\omega_{S,M}$, it is convenient to introduce the spin operator $O_{S,M}$ which projects out the component of the pure spin state:

$$\begin{aligned} \{S^2 - S(S+1)\} O_{S,M} &= 0 \ , \\ \{S_z - M\} O_{S,M} &= 0 \ , \\ \sum_{S,M} O_{S,M} &= 1 \ . \end{aligned} \tag{2.10}$$

We note that this operator works only on the spin part of a wave function. For any wave function

$$\Phi = \sum_i c_i \Psi_i(r_1, r_2, \cdots, r_N)\Theta_i(\sigma_1, \sigma_2, \cdots, \sigma_N) \ ,$$

$O_{S,M}\ \Phi$ is expressed as

$$O_{S,M}\Phi = \sum_i c_i \Psi_i (O_{S,M}\Theta_i) \ .$$

Since the wave function under consideration is an eigenfunction of S_z with the eigenvalue M , we shall drop the subscript M in the following unless it causes some ambiguity.

The weight ω_S for the wave function Φ can be written as

$$\begin{aligned} \omega_S &= \frac{\langle O_S \Phi, O_S \Phi \rangle}{\langle \Phi , \Phi \rangle} = \frac{\langle \Psi\Theta, O_S \mathcal{A} \Psi\Theta \rangle}{\langle \Psi\Theta, \mathcal{A}\Psi\Theta \rangle} \\ &= \frac{\sum_P \varepsilon_P \langle \Psi, P^x \Psi \rangle \langle \Theta, O_S P^\sigma \Theta \rangle}{\sum_P \varepsilon_P \langle \Psi, P^x \Psi \rangle \langle \Theta, P^\sigma \Theta \rangle} \ , \end{aligned} \tag{2.11}$$

where P^x and P^σ denote the corresponding permutations of the space and the spin coordinates respectively. Similarly we obtain the expectation value of a spin-free operator f ,

$$\langle f\rangle_S = \frac{\langle O_S\,\Phi, f\,O_S\,\Phi\rangle}{\langle O_S\,\Phi, O_S\,\Phi\rangle} = \frac{\langle \Psi\Theta, f\,O_S\,\mathcal{A}\,\Psi\Theta\rangle}{\langle \Psi\Theta, O_S\,\mathcal{A}\,\Psi\Theta\rangle}$$

$$= \frac{\sum_P \varepsilon_P \langle \Psi, f\,P^x\Psi\rangle \langle \Theta, O_S\,P^\sigma\Theta\rangle}{\sum_P \varepsilon_P \langle \Psi, P^x\Psi\rangle \langle \Theta, O_S\,P^\sigma\Theta\rangle} \quad . \tag{2.12}$$

We shall derive an explicit formula for $\langle \Theta,\ O_S P^\sigma \Theta \rangle$ in the next section. In sections 4 and 5, the weights ω_S derived from a single Slater determinant are given, and the behaviour of the ω_S-values for large N is discussed.

3. CALCULATIONS OF $\langle \Theta,\ O_S P^\sigma \Theta \rangle$

Because we assumed the form (2.8) for the spin part Θ, for any permutation P we can find a permutation Q(P) which brings Θ and $P^\sigma\Theta$ into the following forms:

$$Q^\sigma\Theta = \alpha(1)\alpha(2)\cdots\alpha(n+M)\beta(n+M+1)\cdots\beta(2n) \equiv f_0 \quad , \tag{3.1}$$

$$\begin{aligned} Q^\sigma P^\sigma\Theta = {} & \alpha(1)\cdots\alpha(n+M-i)\beta(n+M-i+1)\cdots\beta(n+M)\times \\ & \times\alpha(n+M+1)\cdots\alpha(n+M+i)\beta(n+M+i+1)\cdots\beta(2n) \\ \equiv {} & f_i \quad , \qquad (\ 2n = N\ ) \quad . \end{aligned} \tag{3.2}$$

Here the integer i(P) is the number of α-functions in Θ which are changed to β-functions in $P^\sigma\Theta$. The number i(P) is uniquely determined by the given permutation P.

Using the commutability of O_S and Q^σ, we obtain

$$\begin{aligned} \langle \Theta, O_S P^\sigma\Theta\rangle &= \langle Q^\sigma\Theta, Q^\sigma O_S P^\sigma\Theta\rangle \\ &= \langle Q^\sigma\Theta, O_S Q^\sigma P^\sigma\Theta\rangle \\ &= \langle f_0, O_S f_i\rangle \equiv c_{S,i} \quad . \end{aligned} \tag{3.3}$$

In order to calculate the value $c_{S,i}$, it is convenient to divide the total number of electrons into four groups A, B, C and D . A, B, C and D stand for the first $n + M - i$ electrons, the second i electrons, the third i electrons and the last $n + M - i$ electrons, respectively:

A	$1, 2, \ldots, n + M - i$,
B	$n + M - i + 1, n + M - i + 2, \ldots, n + M$,
C	$n + M + 1, n + M + 2, \ldots, n + M + i$,
D	$n + M + i + 1, n + M + i + 2, \ldots, 2n$.

For example when we write CD, this means the combined groups of C and D , i.e. the last $n - M$ electrons.

We introduce the symbol $Y_K(s, m; \mu)$ for one element of an orthonormal complete set of simultaneous spin eigenfunctions of $\mathbb{S}^2$ and $\mathbb{S}_z$ with the eigenvalues $s(s + 1)$ and m respectively. K denotes an electron system which can be any of the groups defined above. μ specifies one of the spin functions with common s and m , to differentiate degenerate functions. We adopt the usual convention for the relative phase of these functions [1]:

$$(\mathbb{S}_x \pm i\,\mathbb{S}_y)\,Y_K(s,m;\mu) = \sqrt{(s \mp m)(s \pm m + 1)}\,Y_K(s, m \pm 1; \mu) . \qquad (3.4)$$

As the element of the set which has the highest eigenvalue of $\mathbb{S}^2$ ($s = N_K/2$, N_K is the number of electrons in the group K), we choose the following function:

$$Y_K(N_K/2, N_K/2) = \alpha\alpha\cdots\alpha . \qquad (3.5)$$

We may drop μ in this case since (3.5) is the only function in the set with the eigenvalues $s = m = N_K/2$. From (3.4) and (3.5), we obtain

$$Y_K(N_K/2, -N_K/2) = \beta\beta\cdots\beta . \qquad (3.6)$$

An orthonormal set of spin functions of the system ABCD can be obtained by coupling Y_{AB} and Y_{CD} in the following manner:

$$\begin{aligned} Y_{ABCD}(s,m;\mu) &= Y_{ABCD}(s,m;\, s's''\mu'\,\mu'') \\ &= \sum_{m'm''} Y_{AB}(s',m';\mu')\,Y_{CD}(s'',m'';\mu'')\times \\ &\quad \times (s',m';s'',m''\,|\,s',s'',s,m) . \end{aligned} \qquad (3.7)$$

Here $(s',m',s'',m'' \mid s',s'',s,m)$ is the vector coupling coefficient [2]:

$$(s',m',s'',m'' \mid s',s'',s,m) = \delta(m'+m''-m)\times$$
$$\times\left[\frac{(2s+1)(s'+s''-s)!(s'-m')!(s''-m'')!(s+m)!(s-m)!}{(s'+s''+s+1)!(s'-s''+s)!(-s'+s''+s)!(s'+m')!(s''+m'')!}\right]^{1/2}\times$$
$$\times\sum_{\nu}(-1)^{\nu+s'-m'}\frac{(s'+m'+\nu)!(s''+s-m'-\nu)!}{\nu!(s'-m'-\nu)!(s-m-\nu)!(s''-s+m'+\nu)!} \qquad (3.8)$$

Since

$$O_{S,M} = \sum_{\mu} Y_{ABCD}(S,M;\mu)\rangle\langle Y_{ABCD}(S,M;\mu), \qquad (3.9)$$

we obtain

$$c_{S,i} = \sum_{\mu}\langle f_0, Y_{ABCD}(S,M;\mu)\rangle\langle Y_{ABCD}(S,M;\mu), f_i\rangle. \qquad (3.10)$$

The functions f_o and f_i are expressed as

$$f_0 = Y_{AB}\left(\frac{n+M}{2},\frac{n+M}{2}\right)\ Y_{CD}\left(\frac{n-M}{2},-\frac{n-M}{2}\right); \qquad (3.11)$$

and

$$f_i = Y_A\left(\frac{n+M-i}{2},\frac{n+M-i}{2}\right)\ Y_B\left(\frac{i}{2},-\frac{i}{2}\right)\times$$
$$\times Y_C\left(\frac{i}{2},\frac{i}{2}\right)\ Y_D\left(\frac{n-M-i}{2},-\frac{n-M-i}{2}\right). \qquad (3.12)$$

Therefore, the terms of the right side of (3.10) vanish except for the following Y_{ABCD}:

$$Y_{ABCD}\left(S,M;\frac{n+M}{2},\frac{n-M}{2}\right)=\sum_{m',m''}Y_{AB}\left(\frac{n+M}{2},m'\right)Y_{CD}\left(\frac{n-M}{2},m''\right)\times$$
$$\times\left(\frac{n+M}{2},m',\frac{n-M}{2},m''\middle|\frac{n+M}{2},\frac{n-M}{2},S,M\right). \qquad (3.13)$$

Here

$$Y_{AB}\left(\frac{n+M}{2}, m\right) = \sum_{m'm''} Y_A\left(\frac{n+M-i}{2}, m'\right) Y_B\left(\frac{i}{2}, m''\right) \times$$

$$\times \left(\frac{n+M-i}{2}, m, \frac{i}{2}, m'' \middle| \frac{n+M-i}{2}, \frac{i}{2}, \frac{n+M}{2}, m\right) \tag{3.14}$$

and

$$Y_{CD}\left(\frac{n-M}{2}, m\right) = \sum_{m'm'} Y_C\left(\frac{i}{2}, m'\right) Y_D\left(\frac{n-M-i}{2}, m''\right) \times$$

$$\times \left(\frac{i}{2}, m', \frac{n-M-i}{2}, m'' \middle| \frac{i}{2}, \frac{n-M-i}{2}, \frac{n-M}{2}, m\right). \tag{3.15}$$

Using (3.8), (3.11), (3.12), (3.13), (3.14) and (3.15), we find

$$C_{S,i} = \langle f_0, Y_{ABCD}\left(S, M; \frac{n+M}{2}, \frac{n-M}{2}\right)\rangle \langle Y_{ABCD}\left(S, M; \frac{n+M}{2}, \frac{n-M}{2}\right), f_i\rangle$$

$$= \left(\frac{n+M}{2}, \frac{n+M}{2}, \frac{n-M}{2}, -\frac{n-M}{2} \middle| \frac{n+M}{2}, \frac{n-M}{2}, S, M\right) \times$$

$$\times \left(\frac{n+M-i}{2}, \frac{n+M-i}{2}, \frac{i}{2}, -\frac{i}{2} \middle| \frac{n+M-i}{2}, \frac{i}{2}, \frac{n+M}{2}, \frac{n+M-2i}{2}\right) \times$$

$$\times \left(\frac{i}{2}, \frac{i}{2}, \frac{n-M-i}{2}, -\frac{n-M-i}{2} \middle| \frac{i}{2}, \frac{n-M-i}{2}, \frac{n-M}{2}, -\frac{n-M-2i}{2}\right) \times$$

$$\times \left(\frac{n+M}{2}, \frac{n+M-2i}{2}, \frac{n-M}{2}, -\frac{n-M-2i}{2} \middle| \frac{n+M}{2}, \frac{n-M}{2}, S, M\right)$$

$$= (2S+1) \frac{(n-M-i)!\, i!}{(n+S+1)!} \sum_v (-1)^{i-v} \frac{(n+M-i+v)!(S-M+i-v)!}{v!(i-v)!(S-M-v)!(n-S-i+v)!} \tag{3.16}$$

$$= (2S+1) \frac{(n-M-i)!(S+M)!}{(S-M)!} \sum_v (-1)^v \frac{\{(S-M+v)!\}^2}{v!(S-M+v-i)!(n-S-v)!(2S+1+v)!}. \tag{3.17}$$

It is convenient to use the expression (3.16) in calculating the values $C_{S,i}$ for some special cases. For example,

$$c_{S,0} = (2S+1)\frac{(n-M)!(n+M)!}{(n+S+1)!(n-S)!} ,$$

$$c_{M,i} = (2M+1)\frac{i!(n+M-i)!}{(n+M+1)!} ,$$

$$c_{n,i} = \frac{(n+M)!(n-M)!}{(2n)!} .$$

4. APPLICATION TO A SINGLE-DETERMINANT WAVE FUNCTION

When a wave function Φ is a single-determinant wave function, the space part $\Psi(\mathbf{r}_1, \mathbf{r}_2, \cdots, \mathbf{r}_N)$ is a product of one-electron functions:

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \cdots, \mathbf{r}_N) = \psi_1(\mathbf{r}_1)\psi_2(\mathbf{r}_2)\cdots\psi_N(\mathbf{r}_N) . \tag{4.1}$$

We denote orbitals associated with α-spins by $\phi_1, \phi_2, \cdots, \phi_{n+M}$ and those with β-spins by $\varphi_1, \varphi_2, \cdots, \varphi_{n-M}$. Without changing the total wave function Φ, we can transform the orbitals $\{\phi\}$ and $\{\varphi\}$ to $\{\phi'\}$ and $\{\varphi'\}$ so that the only overlap remaining is between the pairs ϕ_i' and φ_i' [3]:

$$\left.\begin{aligned}
&\phi_i' = \sum_{j=1}^{n+M} a_{ij}\,\phi_j , \qquad i = 1,2,\cdots,n+M ,\\
&\varphi_i' = \sum_{j=1}^{n-M} b_{ij}\,\varphi_j , \qquad i = 1,2,\cdots,n-M ,\\
&\langle\phi_i', \phi_j'\rangle = \langle\varphi_i', \varphi_j'\rangle = \delta_{ij} ,\\
&\langle\phi_i', \varphi_j'\rangle = \delta_{ij}\sqrt{\lambda_i} , \qquad \lambda_i \geq 0 .
\end{aligned}\right\} \tag{4.2}$$

Using these transformed orbitals for the space part Ψ, we find that the inner product $\langle \Psi, P^x\Psi \rangle$ vanishes except when P^x is a product of some

interchanges of the pairs $\{\phi_i', \varphi_i'\}$. When P interchanges the electrons of t pairs $\{\phi'_{k1}, \varphi'_{k1}\}$, $\{\phi'_{k2}, \varphi'_{k2}\}$, ... , $\{\phi'_{kt}, \varphi'_{kt}\}$, we see that

$$\begin{aligned} \langle \Psi, P^x \Psi \rangle &= \lambda_{k1} \lambda_{k2} \cdots \lambda_{kt} , \\ \varepsilon_P &= (-1)^t , \\ i(P) &= t . \end{aligned} \tag{4.3}$$

It follows from (2.11), (3.3) and (4.3) that

$$\omega_S = \sum_{k=0}^{n-M} (-1)^k A_k \; c_{S,k} , \tag{4.4}$$

where A_k is defined by the coefficients of the polynomial

$$\prod_{k=1}^{n-M} (1 - \lambda_k x) = \sum_{k=0}^{n-M} (-1)^k A_k \, x^k . \tag{4.5}$$

For example,

$$\begin{aligned} A_0 &= 1 , \\ A_1 &= \sum_k \lambda_k , \\ A_2 &= \frac{1}{2} \Big(\sum_k \lambda_k\Big)^2 - \sum_k \lambda_k^2 = \lambda_1\lambda_2 + \lambda_1\lambda_3 + \cdots + \lambda_1\lambda_{n-M} + \\ &\quad + \lambda_2\lambda_3 + \cdots + \lambda_{n-M-1}\lambda_{n-M} , \\ &\vdots \\ A_{n-M} &= \prod_k \lambda_k . \end{aligned}$$

In order to calculate (4.4), it is convenient to introduce the following polynomial W(x) :

$$W(x) = \prod_{k=1}^{n-M} \{1 - (1 - \lambda_k) x \} = \sum_{k=0}^{n-M} (-1)^k B_k \, x^k . \tag{4.6}$$

By comparing (4.5) and (4.6), it is found that

$$A_k = \sum_{j=0}^{k} (-1)^j \frac{(n-M-j)!}{(n-M-k)!(k-j)!} B_j \ . \qquad (4.7)$$

The weights ω_S of a single-determinant wave function are, therefore, expressed as

$$\omega_S = \sum_{k=0}^{n-M} \sum_{j=0}^{k} (-1)^{j+k} \frac{(n-M-j)!}{(n-M-k)!(k-j)!} B_j C_{S,k}$$

$$= (2S+1) \frac{(S+M)!}{(S-M)!} \sum_{\nu=0}^{n-S} \sum_{j=0}^{n-M} \sum_{k=j}^{S-M+\nu} (-1)^{\nu+j+k} \times$$

$$\times \frac{\{(S-M+\nu)!\}^2 (n-M-j)!}{(n-S-\nu)!(2S+1+\nu)!\,\nu!\,(k-j)!(S-M+\nu-k)!} B_j$$

$$= (2S+1) \frac{(S+M)!}{(S-M)!} \sum_{\nu=0}^{n-S} (-1)^{\nu} \frac{\{(S-M+\nu)!\}^2}{(2S+1+\nu)!\ \nu!} B_{S-M+\nu} \ . \qquad (4.8)$$

This can be written as an integral,

$$\omega_S = (-1)^{S-M} \frac{2S+1}{(S-M)!} \int_0^1 x^{S-M} (1-x)^{S+M} \frac{d^{S-M} W(x)}{dx^{S-M}} dx \ . \qquad (4.9)$$

When $W(x)$ is given, we can derive ω_S using the above equation (4.9). *)

---

*) Since the first order density matrix completely determines the original single-determinant wave function, it should also determine the weight ω_S. We derive an explicit expression for $W(x)$ in terms of the first order density matrix. ω_S can be derived from $W(x)$ by using eq. (4.9).

The first order density matrix of the wave function under consideration has the following form:

$$\rho(\xi, \xi') = \rho_+(\mathbf{r}, \mathbf{r}')\alpha(\sigma)\ \alpha(\sigma') + \rho_-(\mathbf{r}, \mathbf{r}')\beta(\sigma)\ \beta(\sigma') \ ,$$

where

$$\rho_+ = \sum_{i=1}^{n+M} \phi_i' \rangle \langle \phi_i' ,$$

$$\rho_- = \sum_{i=1}^{n-M} \varphi_i' \rangle \langle \varphi_i' .$$

Since

$$\langle \varphi_i', \{(1-x)\rho_- + x\rho_-\rho_+\}\varphi_j' \rangle = \delta_{ij}\{1-(1-\lambda_i)x\} ,$$

W(x) can be expressed as an expectation value of an n-M particle operator K(x):

$$W(x) = \langle \Psi^-, K(x)\Psi^- \rangle ,$$

where

$$K(x : \mathbb{I}_1, \mathbb{I}_2, \cdots, \mathbb{I}_{n-M} : \mathbb{I}_1', \mathbb{I}_2', \cdots, \mathbb{I}_{n-M}') =$$
$$= \prod_{i=1}^{n-M} \{(1-x)\rho_-(\mathbb{I}_i, \mathbb{I}_i') + x\,\rho_-\rho_+(\mathbb{I}_i, \mathbb{I}_i')\}$$

and

$$\Psi^-(\mathbb{I}_1, \mathbb{I}_2, \cdots, \mathbb{I}_{n-M}) = \sqrt{(n-M)!}\,\mathcal{A}\varphi_1'(\mathbb{I}_1)\varphi_2'(\mathbb{I}_2)\cdots\varphi_{n-M}'(\mathbb{I}_{n-M}) .$$

It is seen that $\mathcal{A}\,K(0)$ is a projection operator,

$$\mathcal{A}\,K(0) = \Psi^-\rangle\langle\Psi^- ,$$

and $K(0)\,K(x) = K(x)$. Therefore, we obtain an expression of W(x) in terms of ρ_+ and ρ_- only:

$$W(x) = \langle \Psi^-, K(x)\Psi^- \rangle = \mathrm{tr}\,\mathcal{A}K(0)\,K(x) = \mathrm{tr}\,\mathcal{A}K(x) .$$

5. BEHAVIOUR OF ω_S FOR LARGE N

We discuss the case when all λ_k's are equal to λ. Then

$$W(x) = \{1-(1-\lambda)x\}^{n-M}. \tag{5.1}$$

Putting (5.1) into (4.9), we obtain

$$\omega_S(\lambda) = (2S+1)\frac{(n-M)!(1-\lambda)^{S-M}}{(S-M)!(n-S)!}\int_0^1 x^{S-M}(1-x)^{S+M}\{1-(1-\lambda)x\}^{n-S}dx. \tag{5.2}$$

The asymptotic form of (5.2) is derived in the appendix when S - M is small compared with $N^{2/3}$,

$$\omega_S(\lambda) \sim \frac{(2S+1)(n-M)^{S-M}}{(1-\lambda)(n-M+\frac{2M}{1-\lambda})^{S-M+1}}\exp\{-\frac{1}{2(n-M)}(S-M-1)(S-M)-$$

$$-\frac{2M+(1-\lambda)^2(n-M)}{2\{2M+(1-\lambda)(n-M)\}^2}(S-M+1)(S-M+2)-$$

$$-\frac{\lambda}{2M+(1-\lambda)(n-M)}(S-M)(S-M+1)\}. \tag{5.3}$$

The equation (5.3) may be regarded valid over all possible values of S, since both left and right hand sides of (5.3) decrease rapidly as S - M becomes large compared with $N^{1/2}$.

5 a) Orthogonal case

Putting $\lambda = 0$ in the expression (5.2), we obtain

$$\omega_S(0) = (2S+1)\frac{(n+M)!(n-M)!}{(n-S)!(n+S+1)!}. \tag{5.4}$$

It is interesting to note that $\omega_S(0)$ is proportional to the number, $f_{n,S}$, of linearly independent spin functions for given n (= N/2) and S,

$$\omega_S(0) = \frac{f_{n,S}}{\sum_{S'=M}^{n} f_{n,S'}}. \tag{5.5}$$

The asymptotic form of $\omega_S(0)$ is, from (5.3),

$$\omega_S(0) \sim (2S+1)\frac{(n-M)^{S-M}}{(n+M)^{S-M+1}} \exp\left\{-\frac{1}{2(n-M)}(S-M-1)(S-M)-\right.$$
$$\left.-\frac{1}{2(n+M)}(S-M+1)(S-M+2)\right\} . \tag{5.6}$$

For $M = kn\,(0 < k < 1)$, ω_S can be approximated by a geometrical sequence,

$$\omega_S \sim (2S+1)\frac{(n-M)^{S-M}}{(n+M)^{S-M+1}} \sim \frac{2k}{1+k}\left(\frac{1-k}{1+k}\right)^{S-M} \tag{5.7}$$

It should be noted that (5.7) does not contain the number of electrons explicitly. Therefore, for a fixed k, ω_S does not change much when N increases.

For $M = 0$,

$$\omega_S \sim \frac{(2S+1)}{n}\exp\left(-\frac{S^2+S+1}{n}\right) \tag{5.8}$$

From (5.8), the expectation values of S, S^2 and S^3 can be calculated as †)

$$\langle S\rangle = \Sigma\, S\,\omega_S \sim \int \frac{2S^2}{n}\exp(-\frac{S^2}{n})\,dS = \sqrt{n\pi}/2 ,$$

$$\langle S^2\rangle = \Sigma\, S^2\omega_S \sim \int \frac{2S^3}{n}\exp(-\frac{S^2}{n})\,dS = n ,$$

$$\langle S^3\rangle = \Sigma\, S^3\omega_S \sim \int \frac{2S^4}{n}\exp(-\frac{S^2}{n})\,dS = 3\sqrt{n^3\pi}/4 .$$

---

†) The exact values are as follows,

$$\langle S\rangle = \frac{1}{2} + \frac{2^{2n-1}(n!)^2}{(2n)!} ,$$

$$\langle S^2\rangle = n + 1 - \langle S\rangle ,$$

$$\langle S^3\rangle = -\frac{1}{4} + \frac{2^{2n-2}(6n-5)\,n\,(n!)^2}{(2n+1)!} .$$

In figures 1 and 2, ω_S is plotted as a function of S and S/n respectively for N = 10, 100 and 1000, using (5.8). We see from these figures that when N increases, ω_S spreads towards bigger N. However, for large N, appreciable weight ω_S is localized around the value $S_{max} \sim 0.5\sqrt{N}$. The second moment of the distribution around the average $\langle S \rangle$ is

$$\langle S^2 \rangle - \langle S \rangle^2 \sim (1 - \frac{\pi}{4})n \sim 0.107\, N \,.$$

5 b) Non-orthogonal case

For $M \neq 0$,

$$\omega_S(n,M,\lambda) \sim \omega_S\{(1-\lambda)(n-M)+M, M, 0\} \,, \qquad (5.9)$$

since the factor $(2S+1)(n-M)^{S-M}/(1-\lambda)(n-M+2M/1-\lambda)^{S-M+1}$ decreases rapidly compared with the exponential part in (5.3), which may therefore be regarded as 1.

For $M = 0$,

$$\omega_S(n,0,\lambda) \sim \frac{2S+1}{(1-\lambda)n} \exp\left(-\frac{S^2+S+1-\lambda}{(1-\lambda)n}\right)$$

$$\sim \omega_S\{(1-\lambda)n, 0, 0\} \,. \qquad (5.10)$$

It follows from (5.9) and (5.10) that the weight in the non-orthogonal case for N electrons can be approximated by the weight for $2\{(1-\lambda)(n-M)+M\}$ electrons in the orthogonal case:

$$\omega_S(n,M,\lambda) \sim \omega_S\{(1-\lambda)(n-M)+M, M, 0\} \qquad (5.11)$$

When the overlap λ increases, the distribution shrinks. This can be seen from figures 3 and 4, where ω_S for some λ values are plotted as a function of S for $M = 0$ and $M = 0.2\,n$ respectively.

ACKNOWLEDGEMENT

The problem was suggested to us by Professor Per-Olov Löwdin. We would like to thank him for valuable discussions and for his generous hospitality extended to us in Uppsala.

We are indebted to Dr. J.W. Eastman for reading and critisizing the manuscript.

APPENDIX

We define a function I by the integral,

$$I_{\alpha,\beta,\gamma}(z) \equiv \frac{1}{\alpha!}\int_0^1 x^{\alpha}(1-x)^{\beta}(1-zx)^{\gamma}\,dx\,. \tag{A.1}$$

Then the weight (5.2) can be expressed as

$$\omega_S(\lambda) = (2S+1)\frac{(n-M)!(1-\lambda)^{S-M}}{(n-S)!}\,I_{S-M,S+M,n-S}(1-\lambda)\,. \tag{A.2}$$

The maximum of the integrand in (A.1) is given by one of the roots of the following equation,

$$\frac{\alpha}{x_0} - \frac{\beta}{1-x_0} - \frac{z\gamma}{1-zx_0} = 0\,. \tag{A.3}$$

Therefore,

$$x_0 = \frac{(1+z)\alpha+\beta+z\gamma-\sqrt{\{(1+z)\alpha+\beta+z\gamma\}^2-4\alpha z(\alpha+\beta+\gamma)}}{2z(\alpha+\beta+\gamma)}\,. \tag{A.4}$$

The order of x_o is the same as $\alpha/(\beta + z\gamma)$.

Expanding $(1-x)^{\beta}(1-zx)^{\gamma}\exp\frac{\alpha x}{x_o}$ in terms of $x - x_o$, we obtain

$$\begin{aligned}\frac{1}{\alpha!}x^{\alpha}(1-x)^{\beta}(1-zx)^{\gamma} &= \\ &= \{a_0 + a_2(x-x_0)^2 + a_3(x-x_0)^3 + \cdots\}\frac{x^{\alpha}}{\alpha!}\exp(-\alpha x/x_0)\,.\end{aligned} \tag{A.5}$$

Here

$$\begin{aligned} a_0 &= (1-x_0)^{\beta}(1-zx_0)^{\gamma}\exp\alpha\,, \\ a_2 &= -\frac{a_0}{2}\left(\frac{\beta}{(1-x_0)^2} + \frac{z^2\gamma}{(1-zx_0)^2}\right)\,, \end{aligned} \tag{A.6}$$

and

$$a_k = a_0\,O\left(\alpha^{[\frac{k}{2}]}\,x_0^{-[\frac{k}{2}]}\right)\,. \tag{A.7}$$

Integrating (A.5) over the range $(x = 0, x = \infty)$, we arrive at an asymptotic expansion

$$I \sim a_0 b_0 + a_2 b_2 + \cdots \tag{A.8}$$

where

$$b_k = \frac{1}{\alpha!} \int_0^\infty x^\alpha (x - x_0)^k \exp(-\alpha x / x_0) dx , \tag{A.9}$$

$$\left.\begin{aligned} b_0 &= (x_0/\alpha)^{\alpha+1} , \\ b_2 &= b_0 \, x_0^2 (\alpha+2)/\alpha^2 , \end{aligned}\right\} \tag{A.10}$$

$$b_k = b_0 O\left(x_0^k \, \alpha^{-\left[\frac{k+1}{2}\right]}\right) . \tag{A.11}$$

From (A.5), (A.7) and (A.11), we find the order of magnitude of $a_k b_k$:

$$a_k b_k / a_0 b_0 = \begin{cases} O\left(x_0^{\frac{k}{2}}\right) & k : \text{even} , \\ O\left(x_0^{\frac{k-1}{2}} / \beta + z\gamma\right) & k : \text{odd} . \end{cases} \tag{A.12}$$

Remembering that the order of x_o is the same as that of $\alpha/(\beta + z\gamma)$ and using (A.12), we can take the first two terms in (A.8) in order to calculate $\log \omega_S$ with the accuracy of order $(\beta + Z\gamma)^{-1}$. Then we obtain

$$\begin{aligned} I \sim & \left\{1 - \frac{x_0^2 (\alpha+2)}{2\alpha^2} \left\{ \frac{\beta}{(1-x_0)^2} + \frac{z^2 \gamma}{(1 - z x_0)^2} \right\}\right\} \times \\ & \times \frac{x_0^{\alpha+1}}{\alpha^{\alpha+1}} (1 - x_0)^\beta (1 - z x_0)^\gamma \exp \alpha . \end{aligned} \tag{A.13}$$

The expression (A.13) is substituted into (A.2), and after some manipulation, we obtain (5.3).

REFERENCES

1) See, for example, E.U. Condon and G.H. Shortley, The Theory of Atomic Spectra (Cambridge University Press, Cambridge, 1957).

2) See, for example, A.R. Edmonds, Angular Momentum in Quantum Mechanics (Princeton University Press, Princeton, N.J., 1957), p. 44.

3) A.T. Amos and G.G. Hall, Proc. Roy. Soc. A263, 483 (1961).

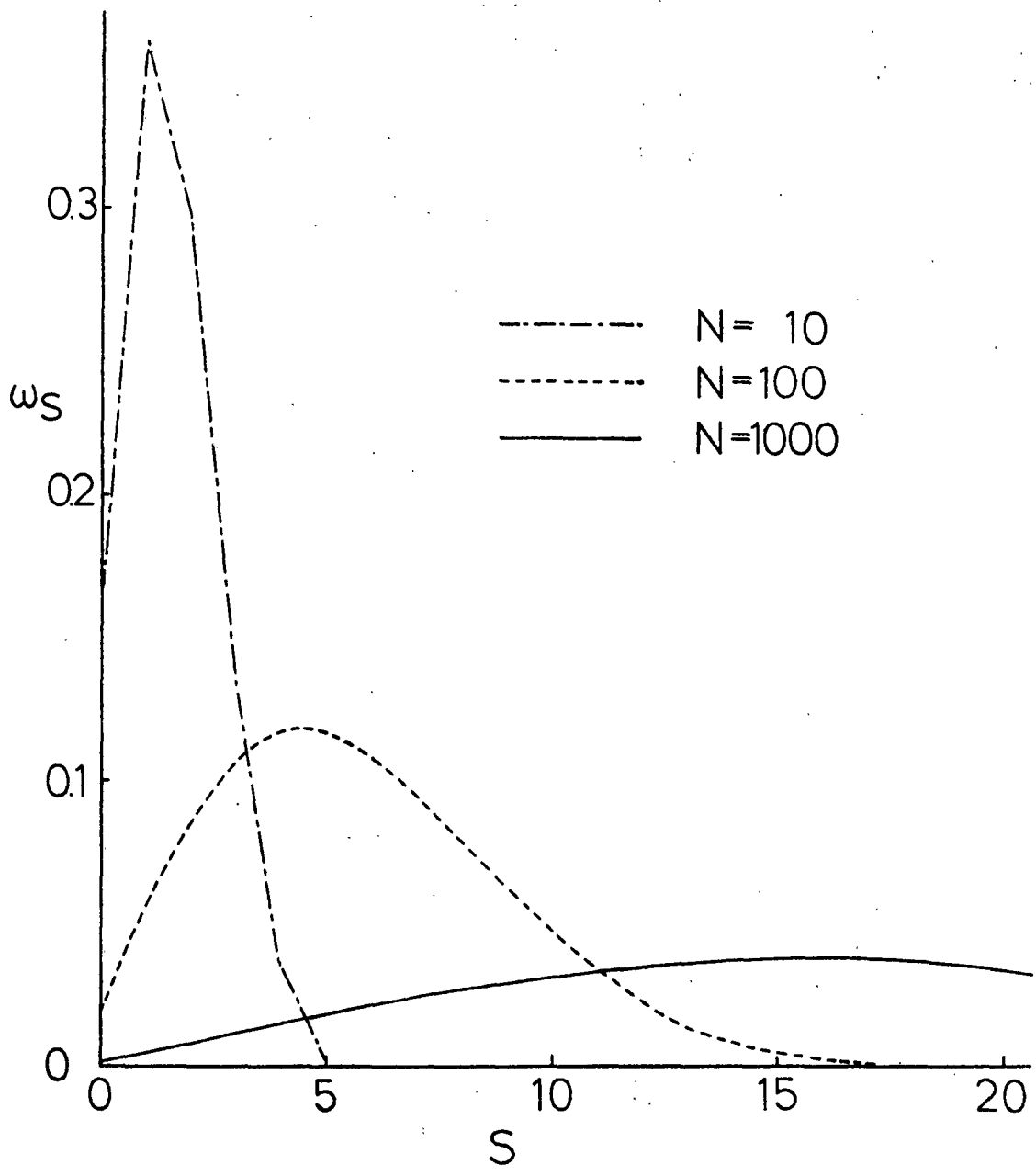

Figure 1. The weights $\omega_s(0)$ as a function of S .

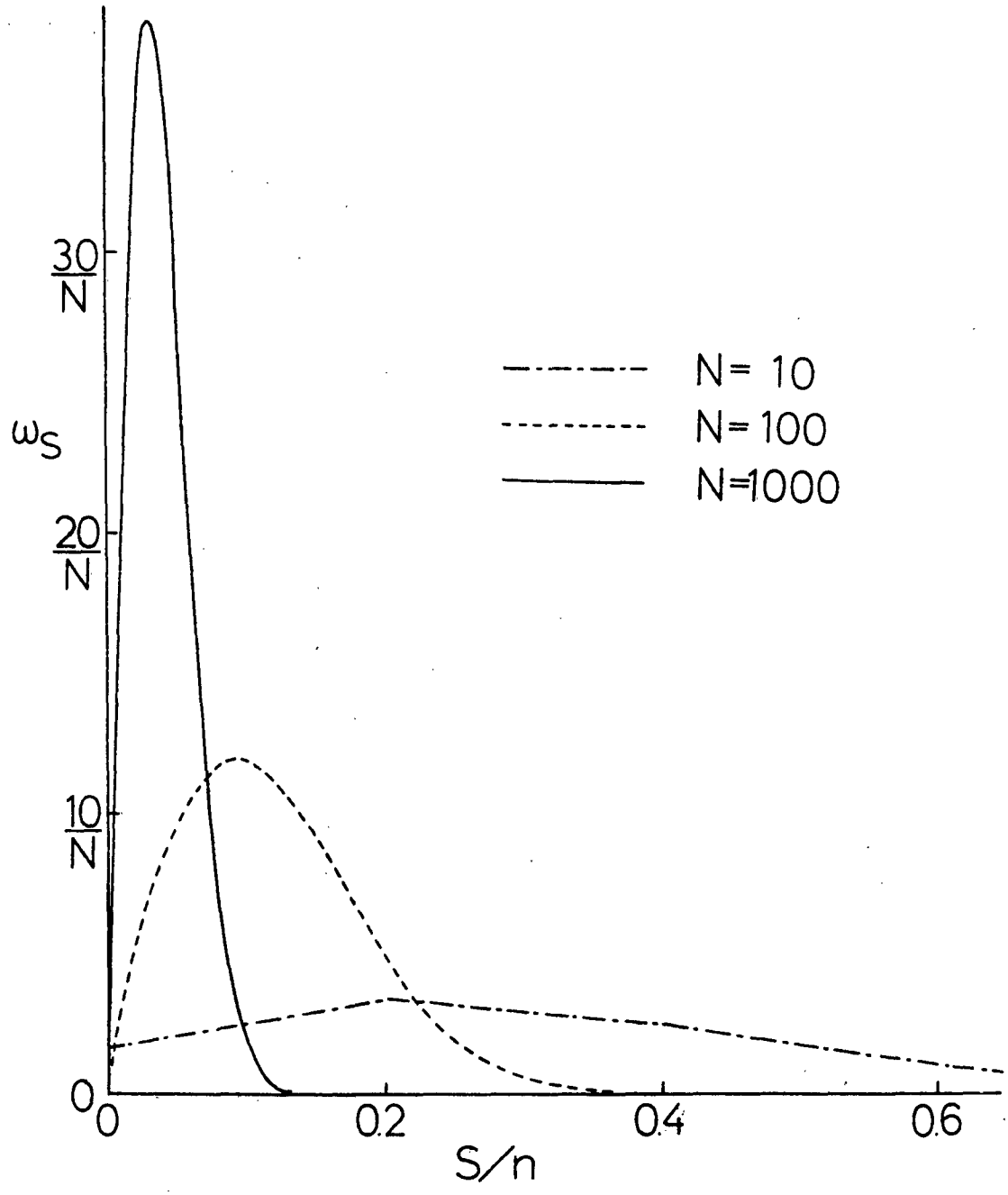

Figure 2 The weights $\omega_s(0)$ as a function of S/n .

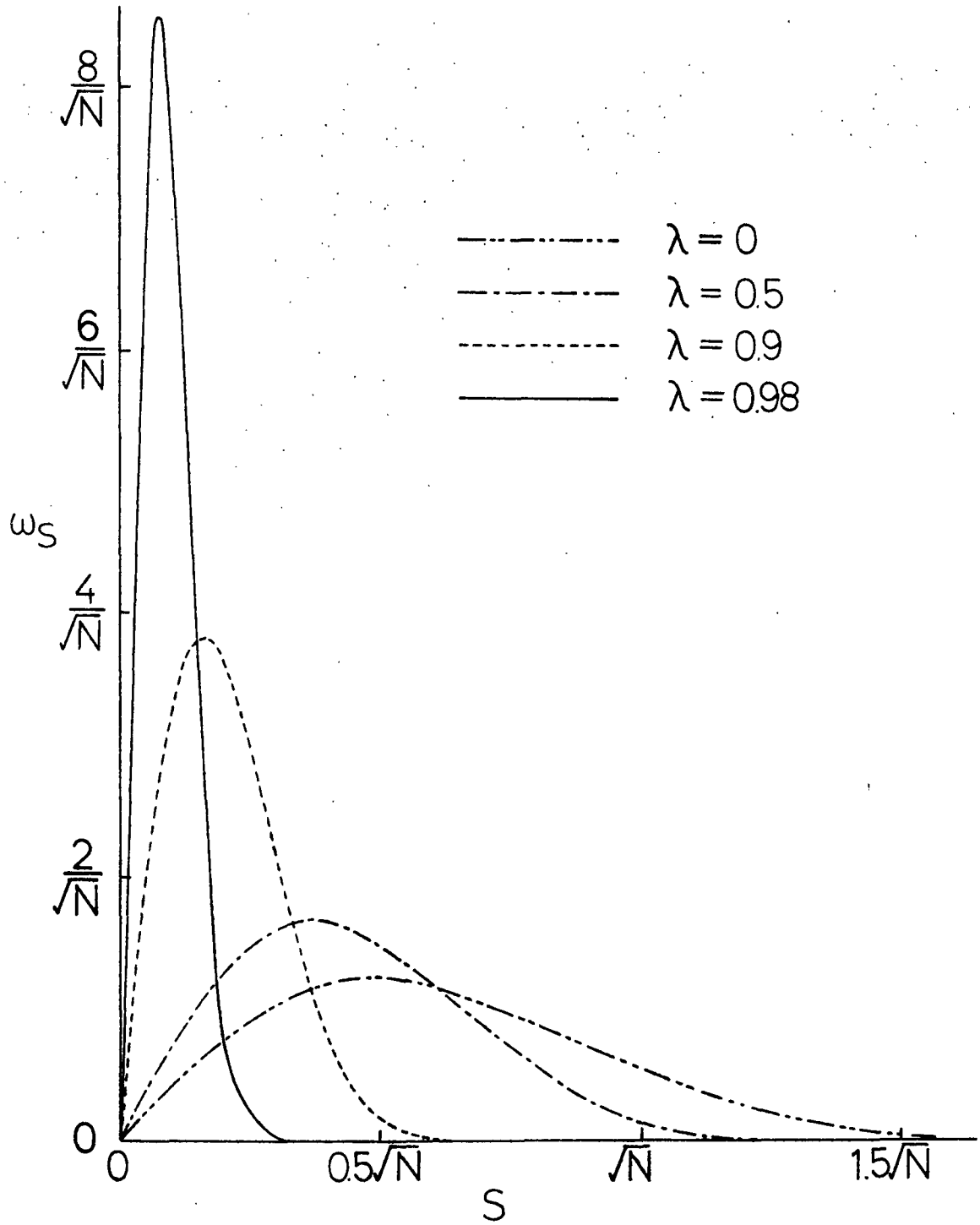

Figure 3 The weights ω_s as a function of S when M = 0 for several values of the overlap integral.

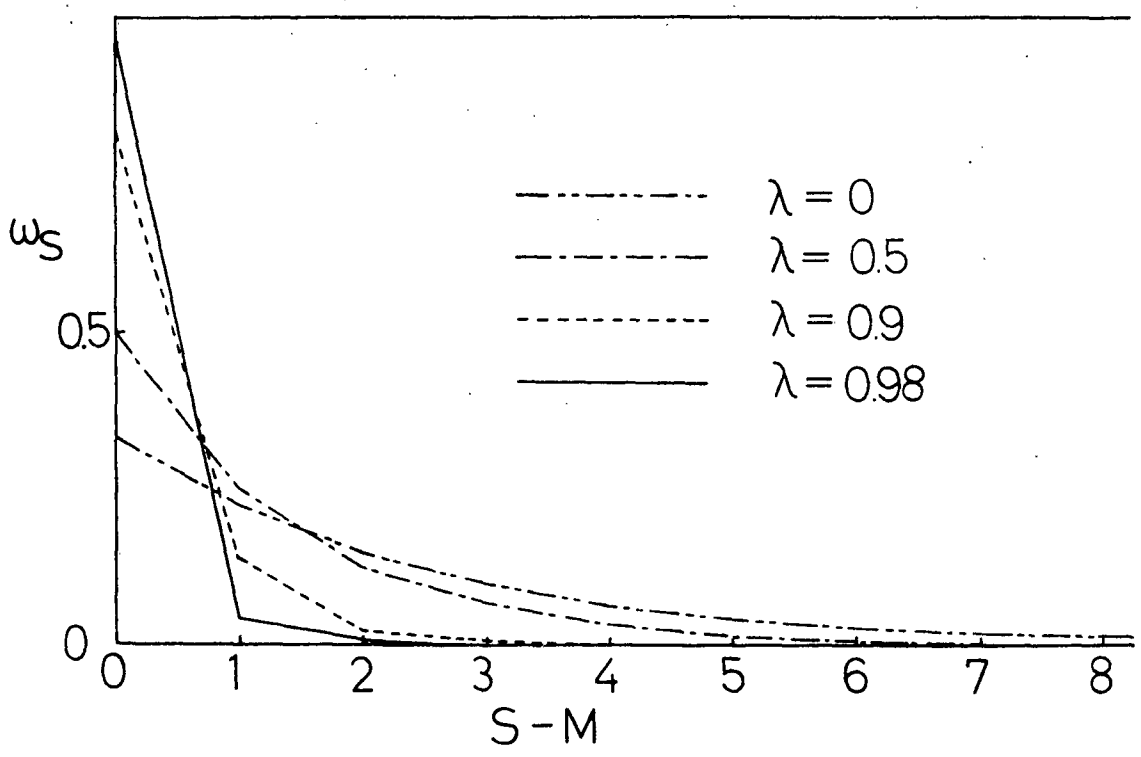

Figure 4 The weights ω_s as a function of S-M when M = 0.2 n for several values of the overlap integral.

RESEARCH REPORTS

List of Technical Notes issued by the Uppsala Quantum Chemistry Group. These Technical Notes are in the United States distributed by "Aeronautical Research Laboratory (RRLC), Wright-Patterson AFB, Ohio". Non-American scientists may obtain copies directly from the Uppsala group.

The mark * indicates that there are no longer any copies available for distribution in Uppsala.

1.	Per-Olov Löwdin and Hiroyuku Yoshizumi	Correlation Problem in Many-Electron Quantum Mechanics. A survey of the Development and a Discussion of some Current Ideas. June 21, 1957. (Published in Advances in Chemical Physics, ed. I. Prigogine 2, 207, 1959).
2.	Per-Olov Löwdin	Spin Degeneracy Problem. July 31, 1957. (Published in Coll. Int. Centre Nat. Rech. Sci. 82, 23, Paris 1958.)
3.	J.O. Hirschfelder and Per-Olov Löwdin	The Long-Range Interaction of Two 1s Hydrogen Atoms Expressed in Terms of Natural Spin Orbitals. August 20, 1957. (Published in Molecular Physics 2, 229, 1959).
4.	Roberto Fieschi and Per-Olov Löwdin	Atomic State Wave Functions Generated by Projection Operators. September 16, 1957.
5.	Anders Fröman	Calculation of Correlation Energies and Relativistic Corrections of some He- and Ne-like Systems. January 15, 1958. (Published in Phys. Rev. 112, 870, 1958).
6.	Per-Olov Löwdin	Scaling Problem, Virial Theorem and Connected Relations in Quantum Mechanics. January 20, 1958. (Published in Mol. Spectroscopy 3, 46, 1959).
7.	Per-Olov Löwdin	Generalization of the Hartree-Fock Scheme. February 20, 1958. (Published in Ann. Acad. Reg. Sci. Upsaliensis 2, 127, 1958).
8.	A.J. Freeman and Per-Olov Löwdin	On a Quantum Mechanical Kinetic Energy Transformation. March 20, 1958. (Published in Phys. Rev. 111, 1212, 1958).
9.	Harrison Shull and Per-Olov Löwdin	Variation Theorem for Excited States. April 1, 1958. (Published in Phys. Rev. 110, 1466. 1958).
10.	Per-Olov Löwdin and Lajos Rédei	Combined Use of the Methods of Superposition of Configurations and Correlation Factor on the Ground States of the Helium-Like Ions. April 15, 1958. (Published in Phys. Rev. 114, 752, 1959).

	11.	Per-Olov Löwdin	An Elementary Iteration-Variation Procedure for Solving the Schrödinger Equation. April 23, 1958. (Acc. for publ. J. Mol. Spect.)
	12.	Per-Olov Löwdin	Angular Momentum Wave Functions Constructed by Projection Operators. May 10, 1958.
	13.	Harrison Shull and Per-Olov Löwdin	Superposition of Configurations and Natural Spin Orbitals. Applications to the He Problem. June 15, 1958. (Published in J. Chem. Phys. 30, 617, 1959).
*	14.	Per-Olov Löwdin	Degeneracies of Atomic dn Configurations Treated by Projection Operator Formalism. July 15, 1958.
*	15.	G.G. Hall	Studies on Molecular Crystals. 1. Excitation on a Pure Crystal. August 1, 1958.
*	16.		Proceedings of a panel meeting on "Correspondence between Concepts in Chemistry and Quantum Chemistry" held at Vålådalen, August 26-30, 1958.
*	17.	Harrison Shull	The Two-Electron Homopolar Chemical Bond; Hydrogen. September 15, 1958.
*	18.		Report from the Summer School in Quantum Chemistry held in Vålådalen, Sweden, July 26 - August 30, 1958, with summaries of four seminars.
*	19.	H. McIntosh	Symmetry-Adapted Functions Belonging to the Symmetric Groups. October 6, 1958. (Published in J. Math. Phys. 1, 453, 1960).
*	20.	G. Del Re	On the Non-Orthogonality Problem in the Semi-Empirical MO-LCAO Method. October 20, 1958. (Published in Nuovo Cimento 17, 644, 1960).
*	21.	H. McIntosh	Towards a Theory of the Crystallographic Point Groups. November 3, 1958. (Published in J. Mol. Spectroscopy 5, 269, 1960).
*	22.	L. Jansen	Symmetry Relations and Electric Multipole Interactions. January 15, 1959.
*	23.	G.G. Hall	Studies on Molecular Crystals. 2. Exciton States of Pure Crystals. February 1, 1959.
*	24.	H. Preuss	The Idea of Atomic Associations in a Simple Form of Perturbation Method. April 20, 1959.
*	25.	J.L. Calais	Derivation of the Clebsch-Gordan-Coefficients by means of Projection Operators. June 1, 195

	26.	Harrison Shull	The Nature of the Two-Electron Chemical Bond. I. The Homopolar Case. June 5, 1959. (Published in J. Am. Chem. Soc. 82, 1287, 1960).
	27.	Per-Olov Löwdin	Some Aspects on the Recent Development of the Theory of the Electronic Structure of Atoms. June 1, 1959. (Presented at the second Robert A. Welch Foundation Conference on Chemical Research, II. Atomic Structure. Houston, Texas, December 1-3, 1958).
	28.	Per-Olov Löwdin	Studies in Perturbation Theory. II. Generalization of the Brillouin-Wigner Formalism. III. Solution of the Schrödinger Equation under a Variation of a Parameter. June 15, 1959.
*	29.	Del Re, Mårtensson and Nordling	A Numerical Investigation Into Some Aspects of the Semi-Empirical MO-LCAO Method. October 1, 1959.
	30.		Report from the International Summer Institute in Quantum Chemistry held at Skogshem, Lidingö, in 1959.
	31.	Z.W. Ritter and R. Pauncz	Approximate Analytical Wave Functions for the 1sns ^1S states of He and He-like Ions. October 15, 1959. (Published in J. Chem. Phys. 32, 1820-1825, 1960).
	32.	J. Linderberg and H. Shull	Electronic Correlation Energy in 3- and 4--Electron Atoms. November 1, 1959. (Published in J. Mol. Spectroscopy 5, 1-16, 1960).
	33.	G.G. Hall	Improved Atomic Wave Functions Using a Functional Transformation. November 20, 1959. (Published in Proc. Phys. Soc. LXXV, 575, 1960).
	34.	A. Fröman	Mass Polarization in He-Like Systems. December 1, 1959.
	35.	P.O. Löwdin	Quantum Theory of Electronic Structure of Molecules. January 1 , 1960. (Published in Ann. Rev. of Physical Chemistry 11, 107, 1960).
	36.	P.O. Löwdin	Expansion Theorems for the Total Wave Function and Extended Hartree-Fock Schemes. February 15, 1960. (Published in Revs. Modern Phys. 32, 328, 1960).
	37.	J. de Heer and R. Pauncz	Molecular Electronic Integrals for Cyclic Systems. February 15, 1960. (Published in J. Mol. Spectroscopy 5, 326, 1960).
	38.	A. Fröman	Relativistic Corrections in Many-Electron Systems. February 15, 1960. (Published in Revs. Modern Phys. 32, 317, 1960).

39.	J.L. Calais and J. Linderberg	Atomic Angular Momentum Wave Functions for the Configurations $s^n p^m$ in the Cases of Weak, Strong and Intermediate Coupling. Studied by the Projection Operator Technique. March 1, 1960.
40.	J. Linderberg	Exact Perturbation Treatment of Hartree--Fock Equations. March 1, 1960. (Published in Phys. Rev. 121, 816, 1961).
41.	Löwdin, Pauncz and de Heer	On the Calculation of the Inverse of the Overlap Matrix in Cyclic Systems. March 15, 1960. (Published in J. Math. Phys. 1, 461, 1960).
42.	A. Fröman and G.G. Hall	The Accuracy of Atomic Wave Functions and Their Scale. March 15, 1960. (Published in J. Mol. Spectroscopy 7, 410-423, 1961).
43.	T. Arai	Theorem on Separability of Electron Pairs. April 1, 1960. (Published in J. Chem. Phys. 33, 95, 1960).
44.	P.O. Löwdin	Note on the Separability Theorem for Electron Pairs. June 15, 1960. (Published in J. Chem. Phys. 35, 78, 1961).
45.	T.L. Bailey and J.L. Kinsey	Test of the Conventional Quantum Chemistry Methods on the Hydrogen Atom. July 1, 1960.
46.	P.O. Löwdin	Exchange, Correlation and Spin Effects in Molecular and Solid-State Theory. July 15, 1960. (Revs. Modern Phys. 34, 80, 1962).
47.	P.O. Löwdin	Studies in Perturbation Theory. IV. Solution of Eigenvalue Problem by Projection Operator Formalism. August 1, 1960. (Published in J. Math. Phys. 3, 969, 1962).
48.	P.O. Löwdin	-----. V. Some Aspects on the Exact Self-Consistent-Field Theory. August 1, 1960. (Publ. in J. Math. Phys. 3, 1171, 1962).
49.	S.O. Lundqvist	On the Possibility of a Modified Perturbation Scheme for Bound States Involving Discrete Sets Only. August 15, 1960.
50.	J.L. Calais and P.O. Löwdin	A Simple Method of Treating Atomic Integrals Containing Functions of r_{12}. September 1, 1960. (Published in J. Mol. Spectroscopy 8, 203-211, 1962).
51.	A. Fröman and P.O. Löwdin	Virial Theorem and Cohesive Energies of Solids, Particularly Ionic Crystals. September 15, 1960. (Published in J. Phys. Chem. Solids 23, 75, 1962).
52.	J.L. Calais	Nuclear State Wave Functions Generated by Projection Operators. October 1, 1960.

53.	A. Fröman and J.L. Kinsey	Variational Treatment of Electronic and Mesonic Hydrogen Molecule Ions. November 1, 1960. (Published in Phys. Rev. 123, 2077, 1961).
54.	A. Fröman	Isotope Effects and Electronic Energy in Molecules. November 1, 1960. (Published in J. Chem. Phys. 36, 1490, 1962).
55.	R. Pauncz, J. de Heer and P.O. Löwdin	Studies on the Alternant Molecular Orbital Method. I. General Energy Expression for an Alternant System with Closed Shell Structure. November 1, 1960. (Published in J. Chem. Phys. 36, 2247, 1962).
56.	R. Pauncz, J. de Heer and P.O. Löwdin	----- . II. Application to Cyclic Systems. November 1, 1960. (Published in J. Chem. Phys. 36, 2257, 1962).
57.	Roy McWeeny	Spin Polarization Effects in Paramagnetic Molecules. November 15, 1960.
58.		Report from the International Summer Institute and Symposium in Quantum Chemistry held at Uppsala University, Uppsala, Sweden, July 17 - August 21, 1960.
59.	Roy McWeeny	On the Non-Orthogonality Problem for Interacting Electronic Systems. January 15, 1961.
60.	Y. Öhrn and R. McWeeny	Justification of the One-Body Model for an Electron Outside a "Core" With Applications to Lithium and Sodium. February 15, 1961.
61.	Roy McWeeny	Perturbation Theory for the Fock-Dirac Density Matrix. March 15, 1961. (Phys. Rev. 126, 1028, 1962).
62.	Z.W. Ritter, R. Pauncz, and K. Appel	Approximate Analytical Wave Functions for the $1s^2ns\ ^2S_{1/2}$ States of Li and Li-Like Ions. April 15, 1961. (Published in J. Chem. Phys. 35, 571-575, 1961).
63.	A. Fröman	Comments on the Relativistic Corrections and the Electronic Correlation in the Li-Like Ions. June 1, 1961.
64.	Per-Olov Löwdin	Studies in Perturbation Theory. VI. Contraction of Secular Equations.
65.	Per-Olov Löwdin	----- . VII. Localized Perturbation.
66.	Klaus Appel	Rational Approximation of Decay-Type Functions. October 1, 1961. (Published in Nordisk Tidskrift for Informationsbehandling, BIT, 2, 69, 1962).
67.	Per-Olov Löwdin	Band Theory, Valence Bond and Tight-Binding Calculations. October 15, 1961. (Published in J. Appl. Phys. 33, 251, 1962).

68.	Per-Olov Löwdin	The Normal Constants of Motion in Quantum Mechanics Treated by Projection Technique. November 15, 1961. (Revs. Modern Phys. 34, 520, 1962).
69.	Jan Olof Nordling	Successive Partitioning Technique for Solution of Secular Equations. December 1, 1961.
70.	William H. Adams	A Hartree-Fock Perturbation Method. December 1, 1961. (Publ. in J. Chem. Phys. 37, 2507, 1962).
71.	Jean-Louis Calais	Permutation Symmetry of the Three-Electron Problem. December 1, 1961.
72.	William H. Adams	The Stability of Hartree-Fock States. December 15, 1961. (Phys. Rev. 127, 1650 (1962)).
73.	Lajos B. Rédei	Remarks on the Quantum Mechanical Interpretation of the Stark Effect in the Hydrogen Atom. December 15, 1961. (Physics Letters 1, 191, 1962).
74.	Jan Linderberg	Study of Atoms by Perturbation Theory. December 15, 1961. (J. Mol. Spectroscopy 9, 95-106, 1962).
75.	Asgar Ali and Richard F. Wood	Applications of localized perturbation technique. April 1, 1962.
76.	William H. Adams	Orbital theories of electronic structure. May 1, 1962. (Publ. in J. Chem. Phys. 37, 2009, 1962).
77.	Fukashi Sasaki	Eigenvalues of Fermion Density Matrices. May 1, 196
78.	Janos Ladik and Klaus Appel	The Energy Band Structure of Polynucleotides in the Hückel Approximation. May 15, 1962.
79.	J. Ladik and K. Appel	Investigation of the π Electron System of Uracil with Different Semiempirical Methods. June 1, 1962.
80.	A.J. Coleman	The Structure of Fermion Density Matrices. June 1, 1962.
81.	Lajos B. Rédei	Limits of error for the electronic density, spin density and atomic form factors in quantum mechanical calculations. July 15, 1962.
82.	Ruben Pauncz	Studies on the Alternant Molecular Orbital Method. IV. Generalization of the Method to States with Different Multiplicities. August 1, 1962. (Publ. in J. Chem. Phys. 37, 2739, 1962).
83.	P.O. Löwdin	Some Recent Progress in the Quantum Theory of Many-Electron Systems. August 15, 1962.
84.	Lars T. Hedin	On the Theoretical Foundation of the One-Electron Approximation. September 1, 1962.

85.	Per-Olov Löwdin	Quantum genetics and the aperiodic solid. Some aspects on the biological problems of heredity, mutations, ageing, and tumors in view of the quantum theory of the DNA molecule. November 11, 1962.
86.	Bernard Pullman and Alberte Pullman	Electronic delocalization and biochemical evolution. November 15, 1962.
87.	Atsushi Tsuchida and Kimio Ohno	"Bond orbital" and "modified electron-pair" calculations on the ammonia molecule. November 15, 1962.
88.		Report from the International Summer Institute in Quantum Chemistry and Solid State Physics, held at the University of Uppsala, Uppsala, Sweden, July 29 - September 1, 1962.
89.	William H. Adams	Correlation effects in the alternant molecular orbital approximation. November 15, 1962.
90.	Fukashi Sasaki and Kimio Ohno	Spin component analysis of single determinant wave functions. November 30, 1962.
91.	Yngve Öhrn and Jan Nordling	On the calculation of some atomic integrals containing functions of r_{12}, r_{13}, and r_{23}. November 30, 1962.
92.	Kimio Ohno, Yukito Tanabe and Fukashi Sasaki	Simple molecular orbital calculations on the electronic structure of iron-porphyrin complexes. November 30, 1962.

T I	G.G. Hall	Permeation through a Spherical Shell. September 20, 1958. (Published in J. Theoret. Biol. 1, 18, 1961).
T II	L. Jansen	Introduction to Statistical Mechanics. February 20, 1959.
T III	L. Hedin and S.O. Lundqvist	Introduction to the Field Theoretical Approach to the Many-Electron Problem. November 15, 1960.
T IV	F. Berencz	Electron Correlation in Calculations on H_2. (Lecture presented at the 3rd International Summer Institute in Quantum Chemistry at Uppsala, Sweden, 1960).
	J.I. Horváth	New Aspects of Quantum Mechanical Theory of the Many-Body Problem. (Lecture presented at the 3rd International Summer Institute in Quantum Chemistry at Uppsala, Sweden, 1960).
T V	A.J. Coleman	A note on nilpotent operators, Jordan canonical form, Segré characteristics and minimal polynomials. (Note prepared for the 4th Internationa Summer Institute in Quantum Chemistry at Uppsala, Sweden 1962.)

Uppsala University, Sweden — Contract:
Quantum Chemistry Dept — AF 61(052)-351
Rep. No. AD — TN 90

Monitoring Agency: USAF, EOOAR — Field: Physics

SPIN COMPONENT ANALYSIS OF SINGLE DETERMINANT WAVE FUNCTIONS.

F. Sasaki and K. Ohno — November 30, 1962

ABSTRACT: Spin components involved in a single Slater determinant were analyzed. Behaviour of the components for a system of large number of particles is discussed.

USAF, European Office, OAR, Brussels, Belgium

Uppsala University, Sweden — Contract:
Quantum Chemistry Dept — AF 61(052)-351
Rep. No. AD — TN 90

Monitoring Agency: USAF, EOOAR — Field: Physics

SPIN COMPONENT ANALYSIS OF SINGLE DETERMINANT WAVE FUNCTIONS.

F. Sasaki and K. Ohno — November 30, 1962

ABSTRACT: Spin components involved in a single Slater determinant were analyzed. Behaviour of the components for a system of large number of particles is discussed.

USAF, European Office, OAR, Brussels, Belgium

Uppsala University, Sweden — Contract:
Quantum Chemistry Dept — AF 61(052)-351
Rep. No. AD — TN 90

Monitoring Agency: USAF, EOOAR — Field: Physics

SPIN COMPONENT ANALYSIS OF SINGLE DETERMINANT WAVE FUNCTIONS.

F. Sasaki and K. Ohno — November 30, 1962

ABSTRACT: Spin components involved in a single Slater determinant were analyzed. Behaviour of the components for a system of large number of particles is discussed.

USAF, European Office, OAR, Brussels, Belgium

Uppsala University, Sweden — Contract:
Quantum Chemistry Dept — AF 61(052)-351
Rep. No. AD — TN 90

Monitoring Agency: USAF, EOOAR — Field: Physics

SPIN COMPONENT ANALYSIS OF SINGLE DETERMINANT WAVE FUNCTIONS.

F. Sasaki and K. Ohno — November 30, 1962

ABSTRACT: Spin components involved in a single Slater determinant were analyzed. Behaviour of the components for a system of large number of particles is discussed.

USAF, European Office, OAR, Brussels, Belgium